

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
30 June 2005 (30.06.2005)

PCT

(10) International Publication Number
WO 2005/059301 A1

(51) International Patent Classification⁷: **E21B 33/13,**
C04B 14/04

Santra [US/US]; 1905 West Walnut, Duncan, OK 73533 (US).

(21) International Application Number:
PCT/GB2004/004899

(74) Agents: WAIN, Christopher, Paul et al.; A A Thornton & Co, 235 High Holborn, London WC1V 7LE (GB).

(22) International Filing Date:
19 November 2004 (19.11.2004)

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/738,199 17 December 2003 (17.12.2003) US

(71) Applicant (*for all designated States except US*): HAL-LIBURTON ENERGY SERVICES, INC. [US/US]; P.O. Box 1431, Duncan, OK 73533 (US).

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for MW only*): WAIN, Christopher, Paul [GB/GB]; A.A. Thornton & Co., 235 High Holborn, London WC1V 7LE (GB).

(72) Inventors; and

Published:

(75) Inventors/Applicants (*for US only*): LUKE, Karen [US/US]; 1403 N. 12th, Duncan, OK 73533 (US). FITZGERALD, Russell, M. [US/US]; 310 Main, Velma, OK 73491 (US). ZAMORA, Frank [US/US]; 2017 Woodcrest Drive, Duncan, OK 73533 (US). ASHOK, K.,

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ZEOLITE-CONTAINING SETTABLE SPOTTING FLUIDS

(57) Abstract: Methods and compositions for wellbore treating fluids, especially settable spotting fluids, that include zeolite and at least one carrier fluid.

WO 2005/059301 A1

to achieve a satisfactory bond between the pipe and the walls of the wellbore because of drilling fluid that remained in the wellbore during primary cementing operations.

Difficulty in removing portions of the drilling fluid is often caused by an increase in the gel strength of the drilling fluid, which is often due to the amount of time the drilling fluid has been left stagnant in the wellbore. In addition, polymeric viscosifiers and additives in the drilling fluid contribute to the formation of a filter cake that is generally very stable and can be difficult to remove. If appreciable drilling fluid and/or filter cake remain in the wellbore or on the walls of the wellbore, a satisfactory bond between the pipe, primary cement and the walls of the wellbore will not be achieved, which can lead to fluid leakage through the annulus and other problems.

Removal of the drilling fluid and filter cake from the wellbore is often attempted by running flushes, washes or spacer fluids through the annulus between the pipe and the walls of the wellbore prior to cementing. Other methods for removing drilling fluid and preventing filter cake from interfering with subsequent primary cementing operations include at least partially displacing the drilling fluid with a settable spotting fluid composition (also referred to as a "settable spotting fluid") before the drilling fluid in the wellbore has had a chance to gain significant gel strength. Conventional settable spotting fluids include a material that sets over time, such as blast furnace slag, fly ash, and similar hydraulic components. Still other methods for achieving satisfactory primary cementing operations when deposits of filter cake are an issue include laying down a filter cake including a settable material on the walls of the wellbore and activating the settable material to set.

The present embodiments provide wellbore treating fluids in the form of settable spotting fluids that include zeolite as a settable material, and methods for causing the zeolite to set and using such settable spotting fluids in drilling operations.

Description

According to embodiments described herein, wellbore treating fluids comprising zeolite are introduced into a wellbore in the form of a settable spotting fluid.

Methods according to the present embodiments provide for introducing a wellbore treating fluid comprising zeolite into a wellbore penetrating a subterranean zone, introducing a subsequent composition comprising a compressive strength-developing amount of an activator into the wellbore to displace all but a remaining portion of the wellbore treating

at least partially displaces mud from a wellbore, portions of the settable spotting fluid remain on the walls of the wellbore as part of the filter cake, and/or in permeable areas affecting the wellbore, such as fissures, fractures, caverns, vugs, thief zones, low pressure subterranean zones or high pressure subterranean zones, even if washes or spacer fluids are introduced into the wellbore subsequent to the settable spotting fluid. According to such an embodiment, a subsequent composition, for example, a drilling fluid, pill, spotting fluid or other mud, which contains at least one activator, is pumped into the wellbore. The subsequent composition is pumped into the wellbore, either after the settable spotting fluid, or after the washes or spacer fluids, if such are used. When the activator in the subsequent composition contacts the settable spotting fluid remaining in the filter cake and/or permeable areas, the activator causes the zeolite therein to set. The activator is present in the subsequent composition in a compressive strength-developing amount, and may be one or more of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof. Selection of the type and amount of an activator(s) largely depends on the type and make-up of the composition in which the activator is contained, and it is within the means of those of ordinary skill in the art to select a suitable type and amount of activator.

According to yet another embodiment where portions of a settable spotting fluid comprising zeolite remain on the walls of the wellbore as part of the filter cake, and/or in permeable areas affecting the wellbore, primary cementing operations are performed by introducing a cement slurry containing at least one activator into the wellbore. The cement slurry can be introduced after the settable spotting fluid to displace the settable spotting fluid from the wellbore, or can be introduced after a wash or spacer fluid that was pumped into the wellbore after the settable spotting fluid. As the cement slurry is pumped, and as it begins to set in the wellbore, the activator therein diffuses into the settable spotting fluid remaining in the filter cake and/or permeable areas, and causes the zeolite to set. The activator is present in the cement slurry in a compressive strength-developing amount, and may be one or more of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof. Selection of the type and amount

fractures, caverns, vugs, thief zones, low pressure subterranean zones or high pressure subterranean zones effectively seals such permeable areas, thereby preventing the entry or flow of formation fluids into the annulus.

Zeolites are porous aluminosilicate minerals that may be either a natural or manmade material. Manmade zeolites are based on the same type of structural cell as natural zeolites, and are composed of aluminosilicate hydrates having the same basic formula as given below. It is understood that as used in this application, the term "zeolite" means and encompasses all natural and manmade forms of zeolites. All zeolites are composed of a three-dimensional framework of SiO_4 and AlO_4 in a tetrahedron, which creates a very high surface area. Cations and water molecules are entrained into the framework. Thus, all zeolites may be represented by the crystallographic unit cell formula:



where M represents one or more cations such as Na, K, Mg, Ca, Sr, Li or Ba for natural zeolites and NH_4 , CH_3NH_3 , $(\text{CH}_3)_3\text{NH}$, $(\text{CH}_3)_4\text{N}$, Ga, Ge and P for manmade zeolites; n represents the cation valence; the ratio of b:a is in a range from greater than or equal to 1 and less than or equal to 5; and x represents the moles of water entrained into the zeolite framework.

Preferred zeolites for use in the wellbore treating fluids of the present embodiments include analcime (hydrated sodium aluminum silicate), bikitaite (lithium aluminum silicate), brewsterite (hydrated strontium barium calcium aluminum silicate), chabazite (hydrated calcium aluminum silicate), clinoptilolite (hydrated sodium aluminum silicate), faujasite (hydrated sodium potassium calcium magnesium aluminum silicate), harmotome (hydrated barium aluminum silicate), heulandite (hydrated sodium calcium aluminum silicate), laumontite (hydrated calcium aluminum silicate), mesolite (hydrated sodium calcium aluminum silicate), natrolite (hydrated sodium aluminum silicate), paulingite (hydrated potassium sodium calcium barium aluminum silicate), phillipsite (hydrated potassium sodium calcium aluminum silicate), scolecite (hydrated calcium aluminum silicate), stellerite (hydrated calcium aluminum silicate), stilbite (hydrated sodium calcium aluminum silicate) and thomsonite (hydrated sodium calcium aluminum silicate). Most preferably, the zeolites for use in the wellbore treating fluids of the present embodiment include chabazite and clinoptilolite.

EXAMPLE 1

Six settable spotting fluids ("Spots") were prepared by combining the components as set forth in TABLE 1 below. Specifically, the zeolite and the hydrated lime were dry-mixed by hand in a glass jar. This dry mix was then added over a 15 second period to a carrier fluid being maintained in a Waring blender at 4,000 RPM. The blender speed was then increased to 12,000 RPM and mixing was continued for 35 seconds.

According to the embodiments illustrated in Table 1, the carrier fluid was water. The amount of hydrated lime and water used to form each settable spotting fluid is reported in the table as a "% bwoZ", which indicates a weight percent based on the weight of the zeolite.

Chabazite was used as the zeolite for Spots 1 – 4, and clinoptilolite was used as the zeolite for Spots 5 – 6. Each of these zeolites is commercially available from C2C Zeolite Corporation of Calgary, Canada.

The compressive strength for each of Spots 1 – 6 was determined by Non-Destructive Sonic Testing as set forth in API Specification 10B 22nd Edition, 1997, of the American Petroleum Institute, the entire disclosure of which is incorporated herein by reference as if reproduced in its entirety. As reported in Table 1, the compressive strength was measured at 160°F at the reported elapsed times. The measured compressive strength is reported in Table 1 in pounds per square inch (psi).

spotting fluids are used.

The compressive strength data also illustrates that settable spotting fluids comprising zeolite and water develop an early compressive strength, which increases over time. This illustrates that the zeolite will set, and is a satisfactory substitute for settable material, such as blast furnace slag, fly ash and other hydraulic materials, used in conventional settable spotting fluids. In the settable spotting fluids of Example 1, setting of the zeolite was caused by the lime, also known as calcium hydroxide, which is a known activator for converting settable material in conventional settable spotting fluids. Thus, when an activator, such as lime, is brought into contact with a wellbore treating fluid comprising zeolite, such as the settable spotting fluids illustrated herein, the activator causes the zeolite to set.

Contact between an activator and a settable material can be accomplished by various methods well known to those of ordinary skill in the art. The addition of the lime and zeolite together in a settable spotting fluid as described in this example simulates two of the various methods suitable for bringing an activator into contact with the zeolite. According to the first method simulated by this example, zeolite from wellbore treating fluids, such as the settable spotting fluids illustrated herein, remains on the walls of the wellbore as part of the filter cake, and/or in permeable areas affecting the wellbore, such as fissures, fractures, caverns, vugs, thief zones, low pressure subterranean zones or high pressure subterranean zones, even if subsequent washes or spacer fluids are used to displace the wellbore treating fluid. An activator is brought into contact with the zeolite remaining in the wellbore by circulation of a subsequent composition, such as a drilling fluid, pill, spotting fluid or other mud, which contains the activator. According to the second method simulated by this example, an activator is brought into contact with the zeolite remaining in the wellbore by diffusion of an activator contained in a cement slurry that is subsequently pumped into the wellbore during primary cementing operations.

The two methods simulated by this example are exemplary only, as a variety of methods for bringing a settable material into contact with an activator, which are well known to those of ordinary skill in the art, are suitable for use with the present embodiments.

Example 2 illustrates yet another method.

Days 5 and 6 as reported in Table 2B were determined. The compressive strengths are reported in Table 2B in pounds per square inch ("psi"). To determine the compressive strength, each of Spots 1, 2 and 3 were placed in sealed cylindrical plastic containers, 2 inches in diameter by 4 inches in height. Each plastic container was placed in a water bath at the temperature reported in Table 2B, under atmospheric pressure, for the time periods reported in Table 2B. Each plastic container was then removed from the water bath, allowed to cool, and the cylindrical samples were demolded. The top end of each cylindrical sample was cut using a tile saw to give a smooth and level surface. The remainder of the sample was then placed in a Tinius Olsen universal testing machine and the compressive strength determined according to operating procedures for the universal testing machine.

TABLE 2B

Gel Strength and Compressive Strength Measured at Temp °F and at Time						
Spot #: Test Temp.	Time Day 1	Time Day 2	Time Day 3	Time Day 4	Time Day 5	Time Day 6
Spot 1: Temp: 140 °F	< 10 lb/100 ft ²	< 10 lb/100 ft ²	< 10 lb/100 ft ²	~ 100 lb/100 ft ²	gel turned to solid	> 250 psi
Spot 2: Temp: 160 °F	< 10 lb/100 ft ²	< 10 lb/100 ft ²	< 10 lb/100 ft ²	gel turned to solid	> 280 psi	not taken
Spot 3: Temp: 190 °F	< 10 lb/100 ft ²	< 10 lb/100 ft ²	< 10 lb/100 ft ²	~ 100 lb/100 ft ²	gel turned to solid	> 230 psi

The gel strength and compressive strength data indicates that wellbore treating fluids

compositions, remedial compositions, well cleanup fluids, workover fluids, spacer fluids, gravel pack fluids, acidizing fluids, fracturing fluids, conformance fluids and the like can be prepared using zeolite and a carrier fluid. Accordingly, improved methods of the present invention comprise preparing a wellbore treating fluid using at least one carrier fluid and zeolite, as previously described herein, and placing the fluid in a subterranean formation. Other methods according to the present embodiments include performing drilling operations, completing and/or stimulating a subterranean formation, and performing primary cementing operations using a wellbore treating fluid comprising zeolite and at least one carrier fluid.

Other embodiments of the current invention will be apparent to those skilled in the art from a consideration of this specification or practice of the invention disclosed herein. However, the foregoing specification is considered merely exemplary of the current invention with the true scope and spirit of the invention being indicated by the following claims.

after the introducing of the drilling fluid.

9. The method of claim 1 wherein the introducing of the subsequent composition comprises:

introducing a cement slurry comprising a compressive strength-developing amount of at least one activator into the wellbore; and

allowing the at least one activator to diffuse into contact with the zeolite in the remaining portion of the wellbore treating fluid.

10. The method of claim 9 wherein the at least one activator is selected from the group consisting of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof.

11. The method of claim 1 wherein the introducing of the subsequent composition comprises:

introducing at least one of a mud, a spotting fluid, a pill and a cement slurry comprising a compressive strength-developing amount of at least one activator into the wellbore.

12. The method of claim 11 wherein the at least one activator is selected from the group consisting of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof.

13. The method of claim 1 wherein the zeolite is represented by the formula:



where M represents one or more cations selected from the group consisting of Na, K, Mg, Ca, Sr, Li, Ba, NH₄, CH₃NH₃, (CH₃)₃NH, (CH₃)₄N, Ga, Ge and P; n represents the cation valence; the ratio of b:a is in a range from greater than or equal to 1 and less than or equal to 5; and x represents the moles of water entrained into the zeolite framework.

14. The method of claim 1, wherein the zeolite is selected from the group consisting of analcime, bikitaite, brewsterite, chabazite, clinoptilolite, faujasite, harmotome, heulandite, laumontite, mesolite, natrolite, paulingite, phillipsite, scolecite, stellerite, stilbite, and thomsonite.

15. The method of claim 1 wherein the at least one carrier fluid comprises a water-based

sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof.

25. The method of claim 19 wherein the at least one retarder is selected from the group consisting of lignosulfonates, citric acids, tartaric acids, gluconic acids, organic acids having an α -hydroxy group, and combinations thereof.
26. The method of claim 19 further comprising placing a cement slurry in the wellbore after the introducing of the subsequent composition.
27. The method of claim 19 wherein the introducing of the subsequent composition comprises introducing at least one of a mud, a spotting fluid, a pill and a cement slurry into the wellbore.
28. The method of claim 27 wherein the subsequent composition comprises at least one activator.
29. The method of claim 28 wherein the at least one activator is selected from the group consisting of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof.
30. The method of claim 19 wherein the zeolite is represented by the formula:

$$M_n[(AlO_2)_a(SiO_2)_b] \cdot xH_2O$$
 where M represents one or more cations selected from the group consisting of Na, K, Mg, Ca, Sr, Li, Ba, NH_4 , CH_3NH_3 , $(CH_3)_3NH$, $(CH_3)_4N$, Ga, Ge and P; n represents the cation valence; the ratio of b:a is in a range from greater than or equal to 1 and less than or equal to 5; and x represents the moles of water entrained into the zeolite framework.
31. The method of claim 19 wherein the zeolite is selected from the group consisting of analcime, bikitaite, brewsterite, chabazite, clinoptilolite, faujasite, harmotome, heulandite, laumontite, mesolite, natrolite, paulingite, phillipsite, scolecite, stellerite, stilbite, and thomsonite.
32. The method of claim 19 wherein the at least one carrier fluid comprises a water-based carrier fluid in an amount of from about 100 to about 200 percent by weight of the zeolite.
33. The method of claim 19 wherein the at least one carrier fluid is selected from the group consisting of water and water-based gels.
34. The method of claim 19 wherein the at least one carrier fluid is selected from the group consisting of fresh water, unsaturated salt solution, brine, seawater, and saturated salt

41. The settable spotting fluid of claim 38 further comprising at least one activator and at least one retarder.
42. The settable spotting fluid of claim 41 wherein the at least one activator is present in a compressive strength-developing amount.
43. The settable spotting fluid of claim 41 wherein the at least one activator is selected from the group consisting of calcium hydroxide, sodium silicate, sodium fluoride, sodium silicofluoride, magnesium silicofluoride, zinc silicofluoride, sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, sodium sulfate, and mixtures thereof.
44. The settable spotting fluid of claim 41 wherein the at least one retarder is selected from the group consisting of lignosulfonates, citric acids, tartaric acids, gluconic acids, organic acids having an α -hydroxy group, and combinations thereof.
45. The method of claim 38 wherein the at least one carrier fluid comprises a water-based carrier fluid in an amount of from about 100 to about 200 percent by weight of the zeolite.
46. The method of claim 38 wherein the at least one carrier fluid is selected from the group consisting of water and water-based gels.
47. The method of claim 38 wherein the at least one carrier fluid is selected from the group consisting of fresh water, unsaturated salt solution, brine, seawater, and saturated salt solution.
48. The method of claim 38 wherein the at least one carrier fluid comprises an oil-based fluid selected from the group consisting of canola oil, kerosene, diesel oil, fish oil, mineral oil, sunflower oil, corn oil, soy oil, olive oil, cottonseed oil, peanut oil and paraffin.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Original Application No

382004/004899

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 1428805	A	16-06-2004	US 2004107877 A1	10-06-2004
			CA 2425019 A1	10-06-2004
			EP 1428805 A1	16-06-2004
			US 2004108113 A1	10-06-2004
			US 2004112600 A1	17-06-2004
			US 2004188091 A1	30-09-2004
			US 2005000734 A1	06-01-2005
			US 2004244977 A1	09-12-2004
			US 2004188092 A1	30-09-2004
US 4888120	A	19-12-1989	DE 3631764 A1	24-03-1988
			AT 63132 T	15-05-1991
			BR 8704798 A	17-05-1988
			CA 1296513 C	03-03-1992
			DE 3769735 D1	06-06-1991
			EP 0260538 A2	23-03-1988
			GR 3001896 T3	23-11-1992
			MX 169678 B	19-07-1993
JP 07003254	A	06-01-1995	JP 2957293 B2	04-10-1999